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| (51) International Patent Classification ⁵ : C07C 25/24, C09K 19/32 C07C 43/225, 255/54, 255/52 | | A1 | (11) International Publication Number: WO 90/08119 (43) International Publication Date: 26 July 1990 (26.07.90) |
| (21) International Application Number: PCT/GB90/00069 (22) International Filing Date: 16 January 1990 (16.01.90) (30) Priority data: 8900870.0 16 January 1989 (16.01.89) GB 8925414.8 10 November 1989 (10.11.89) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Whitehall, London SW6 1TR (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : GRAY, George, William [GB/GB]; Glenwood, Newgate Street, Cottingham, North Humberside HU16 4DZ (GB). TOYNE, Kenneth, Johnson [GB/GB]; 25 Hall Road, Hull, North Humberside HU6 8QW (GB). LACEY, David [GB/GB]; 19 Kildale Close, Hull, North Humberside HU18 9NN (GB). HIRD, Michael [GB/GB]; 22 Anlaby Park Road South, Hull, North Humberside HU18 9NN (GB). | | (74) Agent: BECKHAM, Robert, William; Ministry of Defence, Patents 1A(4) Room 2014, Empress State Building, Lillie Road, London SW6 1TR (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US. Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. | |
| (54) Title: PHENYL NAPHTHALENES HAVING LIQUID CRYSTALLINE PROPERTIES <div style="text-align: center; margin-top: 100px;"> <p style="text-align: right;">(I)</p> </div> | | | |
| (57) Abstract <p>Novel phenyl naphthalenes of general formula (I) wherein R₁ and R₂ are selected from C₁₋₁₅ alkyl, alkoxy, perfluoroalkyl, perfluoroalkoxy and alkynyl, R₁ may also be CN and R₂ may also be fluorine or NCS; m is 0, 1 or 2 provided that if R₁ is alkyl or alkoxy and R₂ is alkyl, alkoxy, perfluoroalkyl or CN then m is 1 or 2. These have liquid crystalline characteristics and may be used as constituents of both nematic and smectic C liquid crystal materials.</p> | | | |

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PHENYL NAPHTHALENES HAVING LIQUID
CRYSTALLINE PROPERTIES

This invention relates to novel phenyl naphthalenes having liquid crystalline properties and to their use in liquid crystal materials and devices.

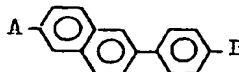
5 Liquid crystal materials and devices exploit the electro-optical properties of nematic or cholesteric (N or N*), or smectic (S) in particular chiral smectic C (Sc*) or smectic A (SA) phases. The most common type of liquid crystal materials in use are those which show a nematic phase and these are extensively used in, for example,
10 watches, clocks, calculators, electronic displays etc.

Liquid crystal materials which show a ferro-electric Sc* phase are useful in fast switching displays such as television or VDU screens as the Sc* phase can be switched in a few milliseconds or even
15 microseconds. The principle of Sc* switching is described inter alia by N A Clark and S T Lagerwall in App-Phys Lett 36 (1980) 899.

Materials which show an SA liquid crystal phase may be used in display devices which exploit the electroclinic effect.
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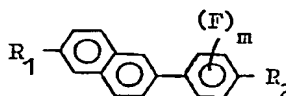
Liquid crystal materials desirably are easy to prepare, show liquid crystal phases which persist over a wide temperature range which preferably includes room temperature and useful physico-chemical properties such as birefringence. For some applications of liquid
25 crystal materials a high birefringence is sought, eg in the so-called "electrically controlled birefringence" (ECB) effect device (see, for example, M F Schieckel and K Fahrenshon App Phys Lett (1971), 19, 2912), in thin film transistors (TFT) or supertwist twisted nematic (STN) devices. It is rare for all the requisite desirable
30 properties to be found in a single liquid crystalline compound and generally liquid crystal materials consist of mixtures of component compounds. Very many liquid crystalline compounds suitable for such uses are known and will be apparent to those skilled in the art.

Some liquid crystalline compounds are known, based upon the phenyl naphthalene system, ie:



5 For example, Bull Soc Chim Fr (1975) 11-12(2) 2521-6 describes compounds where A is alkoxy and B is alkyl or alkoxy and Helv Chim Acta (1985) 68(5) 1406-26 describes those in which A is alkyl or alkoxy and B is cyano or trifluoromethyl. The present inventors have applied developments in synthetic organic chemistry to
10 investigate the phenyl-naphthalene system further with the object of identifying novel compounds which provide improved or alternative liquid crystalline characteristics.

According to this invention, phenyl-naphthalenes of general formula
15 I are provided:



Formula I

wherein R₁ and R₂ are selected from C₁₋₁₅ alkyl, alkoxy, perfluoro-
20 alkyl, perfluoroalkoxy and alkynyl, R₁ may also be CN and R₂ may also be fluorine or NCS, m is 0, 1 or 2 provided that if R₁ is alkyl or alkoxy and R₂ is alkyl, alkoxy, perfluoroalkyl or CN then m is 1 or 2.

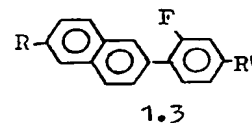
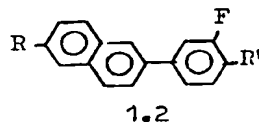
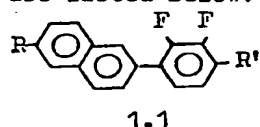
25 The preferred embodiments of the invention discussed below are inter alia chosen with respect to ease of preparation and their liquid crystal properties, particularly with respect to suitability for use in high birefringence nematic or ferro-electric Sc* liquid crystal materials.

30 Preferably for use in nematic materials alkyl or alkoxy substituents R₁ and/or R₂ contain 1-8 carbon atoms and for use in smectic materials 3-12. For use in nematic materials compounds having R₁ as alkyl or alkoxy and R₂ as fluorine; or R₁ as alkynyl and
35 R₂ as alkyl or alkoxy, or R₁ as CN and R₂ as alkyl, alkoxy or alkynyl are preferred. Preferably for smectic C materials R₁ and

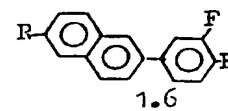
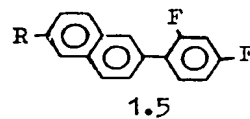
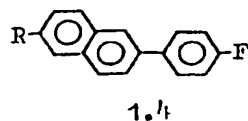
R_2 are selected from n-alkyl or n-alkoxyl, m is 1 or 2, especially 2, preferably with the fluorines in the 2, 3 positions.

Preferred overall structures for the phenyl naphthalenes of formula I are listed below:

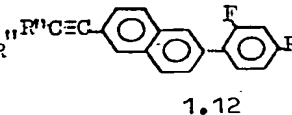
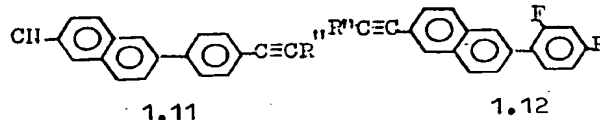
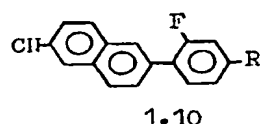
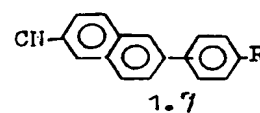
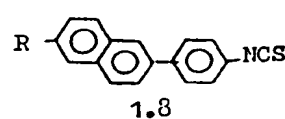
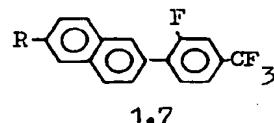
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Where R and R' are independently alkyl or alkoxy and R'' is alkyl.

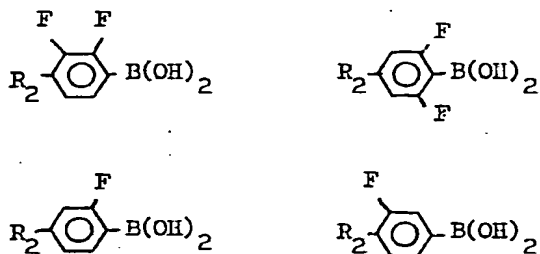
For use in nematic materials structures 1.4, 1.5, 1.6, 1.9, 1.10, 1.11 and 1.12 are preferred. For smectic materials structure 1.1 is preferred.

25

Phenyl-naphthalenes of formula I may be prepared by generally applicable routes A to D shown in Fig 1 of the accompanying drawings. In these routes the reaction conditions of the individual steps are well known but the overall combination of steps to form the end product is novel. Compounds in which R_2 is NCS, eg 1.8 are preferably prepared by initially incorporating an amino group into the molecule as R_2 , for example, coupling the boronic acid of step D1 with para-bromoaniline and then converting the amino group into an isothiocyanate. Ways of doing this will be apparent to those skilled in the art.

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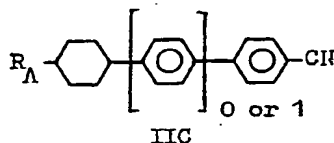
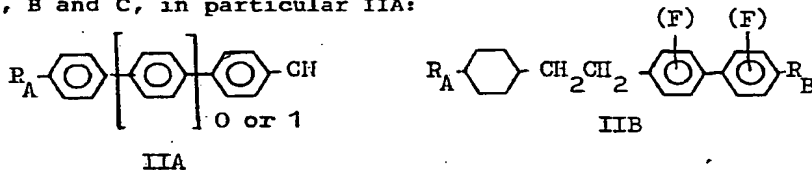
Preparative routes to intermediates of formula:



where R_2 is alkyl or alkoxy are described in published WO 89/02425 and WO 89/08687 among others.

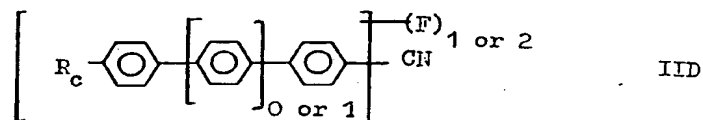
The invention also provides a liquid crystal material being a mixture of at least 2 component compounds, at least one of which is a phenylnaphthalene of formula I. This material may show a nematic or smectic (eg smectic C, S_C^* or S_A) liquid crystal phase.

In particular many phenyl-naphthalenes of formula I have a high birefringence, making them suitable for applications in which this characteristic is required, as discussed above. In particular, compounds of formula I which contain an alkyne group may have a high birefringence. Although some have rather high melting points this can in some cases be usefully reduced by introducing one or more lateral fluorosubstituents on the phenyl ring, eg as in 1.1, 1.2, 1.3, 1.5, 1.6, 1.7, 1.10 and 1.12. Phenyl-naphthalenes of formula I may be used as components of nematic liquid crystal materials together with other known nematic liquid crystalline compounds especially, for example, compounds of general formulae IIA, B and C, in particular IIA:



Where R_A and R_B are independently C_{1-10} n-alkyl or n-alkoxy and (F) indicates that one of the rings carries a fluoro substituent. Other known compounds which may be usefully included as components of nematic liquid crystal materials include those described, for example, in GB 1551043, GB 1556994, GB 1592147, GB 1587819, GB 1603076, GB 2011940, GB 2023136, GB 2027708, GB 2027027, GB 2063250, GB 2063250, GB 2071649, GB 2070594, GB 2071131, GB 2081707, GB 2079275, GB 2080820, GB 2089345, GB-A-8203798, EP 0060646, GB 2111974, US 4482472, GB 2118934, US 4506957, GB 2121406, EP-A-83303348.3, GB 2134110, EP-A-8430494.3, EP-A-84303240.0.

for use in applications where a high birefringence is desirable. The mixture may also contain one or more fluorinated cyanobiphenyls or terphenyls of formula IID:



where R_c is C_{1-10} n-alkyl or n-alkoxyl and the fluoro substituent(s) may be in any one or 2 of the available substitution positions. Compounds of formula IID are known (PCT/GB 89/00647) and their inclusion can further increase the birefringence.

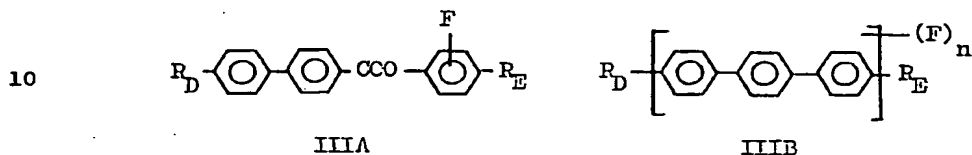
A nematic liquid crystal material of this invention may also contain one or more optically active compounds (especially the biphenyl of formula IIA in which R_A is (+)-2-methylbutyl) to induce a cholesteric phase and one or more pleochroic dyes.

Typically but not exclusively, a nematic liquid crystal material may contain 5-50% by weight of other known nematic materials. Optically active compounds and/or pleochroic dyes if present will generally be present at up to 1% by weight at most.

Phenyl-naphthalenes of formula I may be used as components of smectic C mixtures. Compounds of structure 1.1 above are particularly preferred for this use as they show Sc phases which persist over

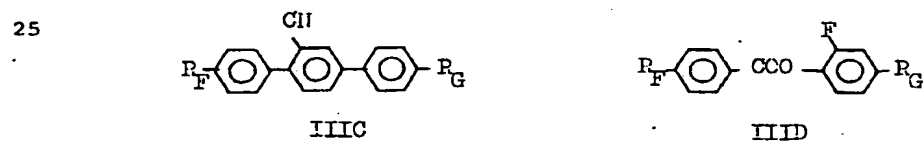
a wide temperature range and their use can result in Sc* mixtures which show fast, eg microsecond, switching speeds.

Other compounds which show an Sc phase to provide a mixture having improved properties relative to the individual component compounds. Preferred known compounds which show an Sc phase and may be used in this way include the known compounds of formula IIIA and IIIB:



where R_D and R_E are independently $\text{C}_3 - \text{C}_{12}$ n-alkyl or n-alkoxy and n in formula IIIB is 1 or 2. In formula IIIA the fluorine substituent is preferably adjacent to the ester linkage. In formula IIIB when n is 1 the fluorine is preferably on the central ring and when n is 2 the fluorines are preferably in the 2, 3- or 2', 3'- positions.

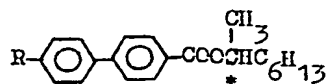
20 The Sc mixture may also include additives which suppress undesirable smectic phases such as S_B , or which promote the phase transition sequence $\text{S}_C - \text{S}_A$ at higher temperatures. Examples of additives which may be used for these purposes are compounds of formula IIIC or IIID:



wherein R_F and R_G are independently $\text{C}_1 - \text{C}_{12}$ n-alkyl or n-alkoxy.

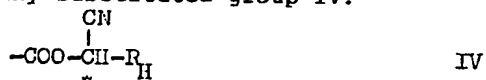
30 When the mixture is intended to show an Sc* phase it is necessary to include one or more optically active compounds, ie "dopants" in the mixture. A large variety of such dopants is known, for example, the compounds described in EP-A-0110299, which are esters of 1-methyleptanol, eg:

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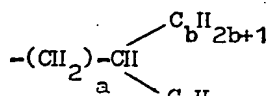


where R is C₁₋₁₅ n-alkyl or alkoxy.

Particularly preferred dopants are however the known compounds containing an asymmetrically substituted group IV:



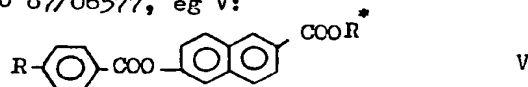
where R_H is cycloalkyl, a cyclic terpenoid ring system or C₁₋₈ n-alkyl or branched alkyl, especially C₁₋₄ n-alkyl or branched alkyl having a formula:



where a is 0 or an integer 1-6 and b and c are independently 1-6. In such compounds R_H is preferably methyl, CH(CH₃)₂ or a camphor residue.

Suitable and preferred examples of such dopants are described in WO 87/07890 and PCT/GB 88/01111.

Another preferred class of optically active dopants are the naphthyl esters disclosed in WO 87/06577, eg V:



where R_I is C₁₋₁₂ n-alkyl or n-alkoxy and R* is 1-methyloheptyl.

Advantageously the Sc* mixture may contain at least 2 optically active dopants having opposite helical twisting effects.

Typically but not exclusively, a ferroelectric Sc* mixture of this invention may contain 1-99% by weight of compounds of formula I, plus 0-99% by weight of other compounds which show an Sc phase, plus 0-30% by weight of additives, plus 1-20% by weight of optically active compounds.

Liquid crystal materials of the invention may be used in display devices of known construction and method of operation. Typically an electro-optical display device will consist of 2 substrates

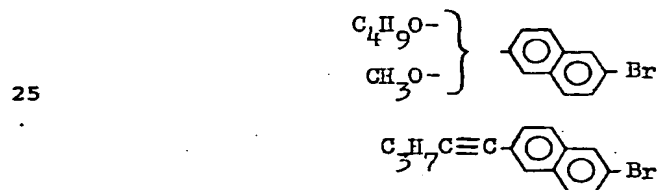
between which a layer of the liquid crystal material may be sandwiched. At least one of the substrates is optically transparent and both have electrodes which are preferably made of a transparent material on their opposing faces. By applying an electric field across the layer of liquid crystal material via the electrodes an electro-optic effect is achieved which may be viewed directly or preferably through one or more polarising filters.

Having a high birefringence nematic materials of this invention may be particularly suitable for use in ECB effect devices. They may also be particularly suitable for use in polymer dispersed liquid crystal (PDLC) materials in which small droplets of a liquid crystal material are dispersed within a matrix of a transparent polymer.

Non-limiting examples illustrating this invention are now described with reference to Fig 1 which shows schematic routes A, B, C and D to phenylnaphthalenes of formula I.

In each synthesis drying was by magnesium sulphate.

Example 1 - Route A Used To Prepare



Step A1 (R = butyl)

30 A solution of 1-bromobutane (50g 0.36 mol) in acetone (90 ml) was added dropwise to a stirred refluxing mixture of 2-hydroxy - 6-bromonaphthalene (40 g 0.18 mol) and potassium carbonate (51 g 0.37 mol) in acetone (1L). The stirred mixture was heated under reflux for 24 hours. The potassium carbonate was filtered off, water was added to the filtrate and the product was extracted into ether (twice). The combined ethereal extracts were washed with

water, 5% sodium hydroxide, water and dried. The solvent and the excess of 1-bromobutane were removed in vacuo to yield an off-white powder which was recrystallised from ethanol. Yield 32.2 g (64%) mp 52-53°C.

5

In an alternative method where R = methyl, dimethyl-sulphate (33.80 g 0.268 mol) was added to a stirred solution of 2-hydroxy - 6-bromonaphthalene (50 g 0.224 mol) and potassium hydroxide (15 g 0.268 mol) in water at room temperature. The stirred mixture was heated at 70°C for one hour and stirred at room temperature over night. The produce was filtered off, washed with 10% sodium hydroxide, water and dried well and then extracted into dichloromethane. The organic extract was washed with 10% sodium hydroxide, water and dried. The solvent was removed in vacuo to give a colourless solid. Yield 50.9 g (96%) mp 108-110°C.

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Step A2

A solution of N-phenyltriflamide (4.93 g 0.0138 mol) in dry dichloromethane (25 ml) was added dropwise to a stirred, cooled (-78°C) solution of 2-hydroxy - 6-bromonaphthalene (2.80 g 0.0126 mol) in dry dichloromethane (40 ml) and dry triethylamine (2.55 g 0.025 mol) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight and was then washed with aqueous sodium carbonate and the separated aqueous layer was washed with dichloromethane. The combined organic extracts were washed with water and dried. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel/ dichloromethane) to give a colourless solid. Yield 7.20 g (99%) mp 93-94°C.

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Step A3

A solution of n-butyllithium (6 ml 2.5 m in hexane) was added dropwise to a stirred, cooled (-5 to 0°C) solution of pent-1-yne (1.02 g 0.015 mol) in dry THF (10 ml) under dry nitrogen. This mixture

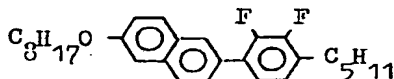
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was stirred at room temperature for 15 minutes and a solution of 6-bromonaphth-2-yl triflate (from Step A2) (4.80 g 0.0135 mol) in dry THF (20 ml) was added dropwise at -5 to 0°C followed by the addition of tetrakis (triphenylphosphine) palladium (0) ("TTPP") (0.5 g 0.43 mmol). The mixture was heated under reflux (90°C for 4 hours) and then poured into 10% hydrochloric acid. The product was extracted into ether (twice) and the combined ethereal extracts were washed with aqueous sodium hydrogen carbonate and dried. The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C) to give a colourless solid. Yield 2.10 g (57%).

This product could be used directly in Steps B1, C1 and D1 or could be reduced using known methods to convert the alkynyl group to an alkyl group.

Example 2 - Route B Used To Prepare



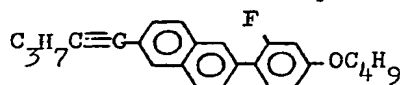
Step B1

A solution of 2-octyloxy - 6-bromonaphthalene (1.75 g 5.22 mol) prepared via Step A1 above in ethanol (15 ml) was added to a stirred solution of 1-pentyl-2, 3-difluoro phenylboronic acid (known) (1.60 g 7.02 mmol) and TTPP (0.312 g 0.27 mol) in benzene (30 ml) and 2 M sodium carbonate (30 ml) at room temperature under dry nitrogen. The stirred mixture was heated under reflux (100°C) for 23 hours. The product was extracted twice into ether and the combined ethereal extracts were washed with brine and dried. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C) -dichloromethane 10:1) to give a colourless solid which was recrystallised from ethanol-ethyl acetate (20:1) to yield colourless crystals. Yield 1.90 g (83%).

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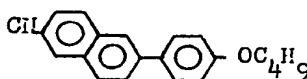
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By an analogous procedure the compound



was prepared, using the product of Step A3 and known 1-butyloxy-3-fluorophenylboronic acid. Yield 63%.

Example 3 - Route C Used To Prepare



10 Step C1

A mixture of 2-methoxy-6-bromonaphthalene (12 g 0.051 mol) and copper (I) cyanide (5.26 g 0.059 mol) in dry DMF (75 ml) was heated at 185°C for 5 hours. The cooled mixture was poured into 10% hydrochloric acid and the product was extracted into ether. The insoluble salts were filtered off and the separated aqueous layer was washed with brine and dried. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C) -dichloromethane 1:2) to give a pale yellow solid. Yield 7.60 g (81%) mp 103-104°C.

Step C2

A solution of boron tribromide (24 g 10.0 ml 0.0956 mol) in dry dichloromethane 200 ml was added dropwise to a stirred, cooled (-78°C) solution of the product of Step C1 (6.90 g 0.0377 mol) in dry dichloromethane (125 ml) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight. Water was carefully added and a yellow precipitate was produced. The product was extracted twice into ether and the combined organic extracts were washed with water and dried. The solvent was removed in vacuo. Yield 6.40 g (100%) mp 156-157°C.

Step C3

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The procedure was as described for Step A2 above. Quantities:

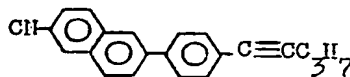
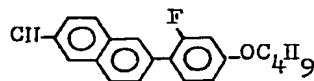
N-phenyltriflamide (9 g 0.024 mol), product of Step C2 (4 g 0.024 mol), trichthylamine (4.9 g 0.049 mol). Yield 7.20 g (99%) mp 93-94°C.

5 Step C4

The procedure for the boronic acid coupling step was as for Step B1 using the product of Step C3 instead of the bromonaphthalene and lithium chloride was added with the TTPP. Quantities: product
10 of Step C3 (0.53 g 1.76 mmol), 4-n-butyloxyphenylboronic acid (0.45 g 2.32 mmol) prepared as on Page 30-31 of WO 89/02425, TTPP (0.13 g 0.11 mmol), lithium chloride (0.22 g 5.22 mmol). The crude product was purified by column chromatography (silica gel/petroleum
15 fraction (bp 40-60°C) -dichloromethane 1:1) to give a colourless solid which was recrystallised from hexane-dimethoxyethane ((1:1) to yield colourless crystals. Yield 0.30 g (58%).

By analogous methods the compounds:

20



25

were prepared. The 4-butyloxy-2-fluorophenylboronic acid was prepared as described on Page 34-35 of WO 89/02425. The 4-pent-1-ynylphenylboronic acid was prepared as below.

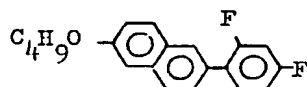
30

A solution of n-butyllithium (7.8 ml 10 M in hexane 0.078 mol) was added dropwise to a stirred, cooled (-5 to 0°C) solution of pent-1-yne (5.28 g 0.078 mol) in dry THF (50 ml) under dry nitrogen. This mixture was stirred for 10 minutes and then a solution of
dry zinc chloride (10.80 g 0.079 mol) in dry THF (100 ml) was added
dropwise at -5 to 0°C. The mixture was stirred at room temperature
for 15 minutes and a solution of para-iodobromobenzene (5.28 g
0.078 mol) in dry THF (100 ml) was added dropwise at -5 to 0°C
35 followed by the addition of TTPP (2.31 g 2.0 mmol). The mixture was stirred overnight and then poured into 10% hydrochloric acid.

The product was extracted twice into ether and the combined ethereal extracts were washed with aqueous sodium hydrogen carbonate and dried. The solvent was removed in vacuo. Yield 14.20 g (82%).

- 5 This 1-bromo-4-pent-1-ynylbenzene (13.45 g 0.06 mol) into the boronic acid in 91% yield using the same method as used in Step 1B on Page 31 of WO 89/02425. Quantities: magnesium (1.7 g 0.07 mol), tri-isopropyl borate (23 g 0.12 mol).

10 Example 4 - Route D Used To Prepare



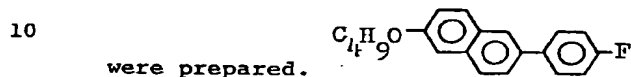
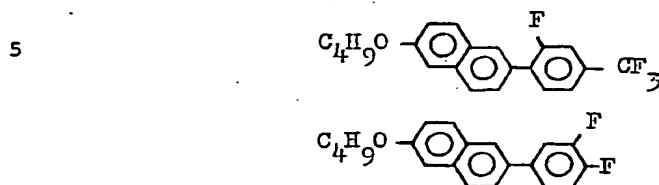
Step D1

- 15 N-butyllithium (12.40 ml 2.5 M in hexane 0.031 mol) was added dropwise to a stirred, cooled (-78°C) solution of 2-bromo-6-butoxy-naphthalene (from Step A1) (8.60 g 0.031 mol) in dry THF (60 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 2.5 hours and then a previously cooled solution
- 20 of tri-isopropyl borate (12 g 0.064 mol) in dry THF (50 ml) was added dropwise at -78°C. The mixture was allowed to warm to room temperature overnight and then stirred for one hour with 10% hydrochloric acid (80 ml). The product was extracted twice into ether and the combined ethereal extracts were washed with water and dried.
- 25 The solvent was removed in vacuo to yield a colourless solid. Yield 8.5 g (100%).

Step D2

- 30 The coupling of the boronic acid (2.27 g 9.30 mmol) from Step D1 with 1-bromo-2,4-difluorobenzene (known) (1.37 g 7.10 mmol) was carried out as for Step B1 above using TPP (0.26 g 0.23 mmol). The product was recrystallised from ethanol to yield colourless crystals. Yield 1.40 g (63%).

Using analogous procedures and known 4-bromo-3-fluoro-trifluoromethyl benzene, 1-bromo-3,4-difluorobenzene and para-bromofluorobenzene the compounds:



Example 5 - Properties of Compounds Prepared

Table 1

15

R₁ R₂ m n Liquid Crystal Transitions (°C)

| | | | | | | |
|----|------|-------------------------------------|-----------------------------------|---|---|---|
| 20 | 1.1* | n-C ₈ H ₁₇ O | n-C ₅ H ₁₁ | 1 | 1 | K 36 Sc 44.5 S _A 75 N 83.5 I |
| | 1.4 | n-C ₄ H ₉ O | F | 0 | 0 | K 128.5 (N 112.9) I |
| | 1.5 | n-C ₄ H ₉ O | F | 1 | 0 | K 72 (N 63.0) I |
| | 1.6 | n-C ₄ H ₉ O | F | 0 | 1 | K 81.5 N(42.0) I |
| | 1.7 | n-C ₄ H ₉ O | CF ₃ | 1 | 0 | K 73.5 S _A 105.5 I |
| 25 | 1.12 | n-C ₃ H ₇ C≡C | n-C ₄ H ₉ O | 1 | 0 | K 68.5 N 106.5 I |

*This compound showed a birefringence $\Delta n = 0.19$ at 20°C.

Table 2

30

Liquid Crystal Transitions (°C)

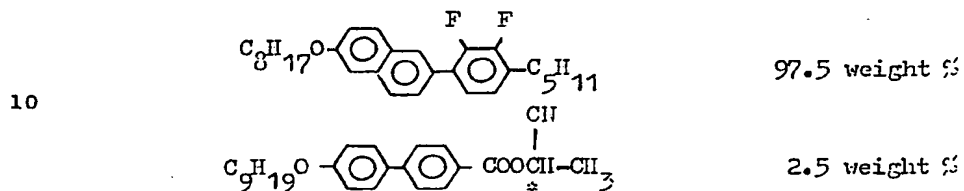
35

| | | | |
|------|----------------------------------|---|------------------|
| 1.9 | OC ₄ H ₉ | 0 | K 98.5 N 167.5 I |
| 1.10 | OC ₄ H ₉ | 1 | K 64.5 N 129.5 I |
| 1.11 | C≡CC ₃ H ₇ | 0 | K 113 N 193 I |

These properties indicate that phenylnaphthalenes of formula I have useful nematic and/or smectic C liquid crystalline properties, showing these useful phases over a broad temperature range.

5 Example 6 - Ferro-electric Sc* Liquid Crystal Mixture

A mixture was prepared having the composition:



This mixture showed the liquid crystal transitions:

15 K 5 Sc* 33 S_A 75 N 80.5 I

The mixture showed spontaneous polarisation Ps (nC cm⁻²) and Sc* cone angles as listed below:

20

Table 3

| | <u>Temp (°C)</u> | <u>Ps (nC cm⁻²)</u> | <u>Cone Angle (°)</u> |
|----|------------------|--------------------------------|-----------------------|
| | 32 | 0.1 | 3.5 |
| 25 | 30 | 1.3 | 6.5 |
| | 28 | 1.8 | 8.5 |
| | 25 | 2.2 | 10.5 |
| | 20 | 2.8 | 11 |
| | 18 | 2.9 | |
| 30 | 15 | 3.1 | |
| | 10 | 3.3 | |
| | 5 | 3.5 | |

Using a 2.0 μm cell at 25°C the switching speed of this mixture was measured as below:

35

16

Table 4

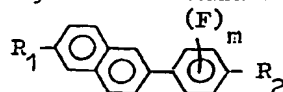
| | <u>Voltage (V peak)</u> | <u>Response Time (μ sec)</u> |
|----|-------------------------|---|
| 5 | 20 | 120 |
| | 30 | 76 |
| | 40 | 54 |
| | 50 | 45 |
| | 60 | 37 |
| 10 | 70 | 32 |

The mixture is therefore a fast switching ferro-electric Sc* material showing a room temperature Sc* phase.

15

CLAIMS

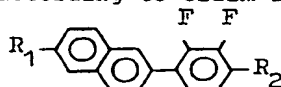
1. Phenylnaphthalenes of general formula I:



formula I

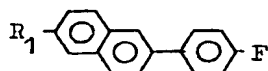
wherein R_1 and R_2 are selected from C_{1-15} alkyl, alkoxy, perfluoroalkyl, perfluoroalkoxy and alkynyl, R_1 may also be CN and R_2 may also be fluorine or NCS; m is 0, 1 or 2 provided that if R_1 is alkyl or alkoxy and R_2 is alkyl, alkoxy, perfluoroalkyl or CN then m is 1 or 2.

2. Phenylnaphthalenes according to Claim 1 characterised in that R_1 and R_2 are independently selected from alkyl and alkoxy and m is 1 or 2.
3. Phenylnaphthalenes according to Claim 2 characterised by a formula:

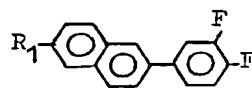
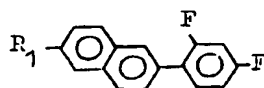


4. Phenylnaphthalenes according to Claim 1 characterised in that R_1 is alkyl or alkoxy and R_2 is fluorine.

5. Phenylnaphthalenes according to Claim 4 characterised by a formula:

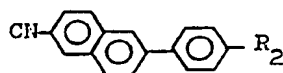


6. Phenylnaphthalenes according to Claim 4 characterised by a formula selected from:



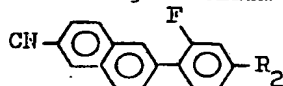
7. Phenylnaphthalenes according to Claim 1 characterised in that R_1 is CN and R_2 is alkyl, alkoxy or alkynyl.

8. Phenylnaphthalenes according to Claim 7 having a formula:



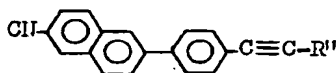
where R_2 is alkyl or alkoxy.

9. Phenyl naphthalenes according to Claim 7 having a formula:



where R_2 is alkyl or alkoxy.

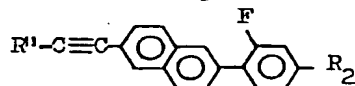
10. Phenyl naphthalenes according to Claim 7 having a formula:



wherein R' is alkyl.

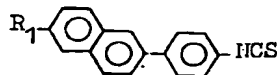
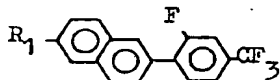
11. Phenyl naphthalenes according to Claim 1 characterised in that R_1 is alkynyl and R_2 is alkyl or alkoxy.

12. Phenyl naphthalenes according to Claim 11 having a formula:



wherein R_2 is alkyl or alkoxy.

13. Phenyl naphthalenes according to Claim 1 having a formula selected from:

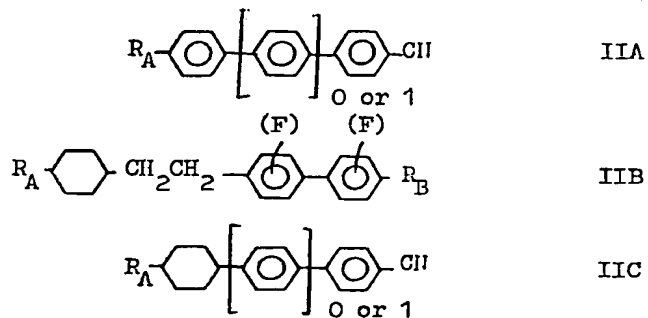


wherein R_1 is alkyl or alkoxy.

14. Liquid crystal material being a mixture of at least 2 component compounds, at least one of which is phenyl naphthalene of formula I as claimed in Claim 1.

15. Liquid crystal material according to Claim 14 characterised in that it is a nematic material that contains 5-50 weight % of phenyl naphthalene(s) of formula I in which R_1 is alkyl or alkoxy and R_2 is fluorine, or R_1 is alkynyl and R_2 is alkyl or alkoxy, or R_1 is OH and R_2 is alkyl, alkoxy or alkynyl, and in that the material

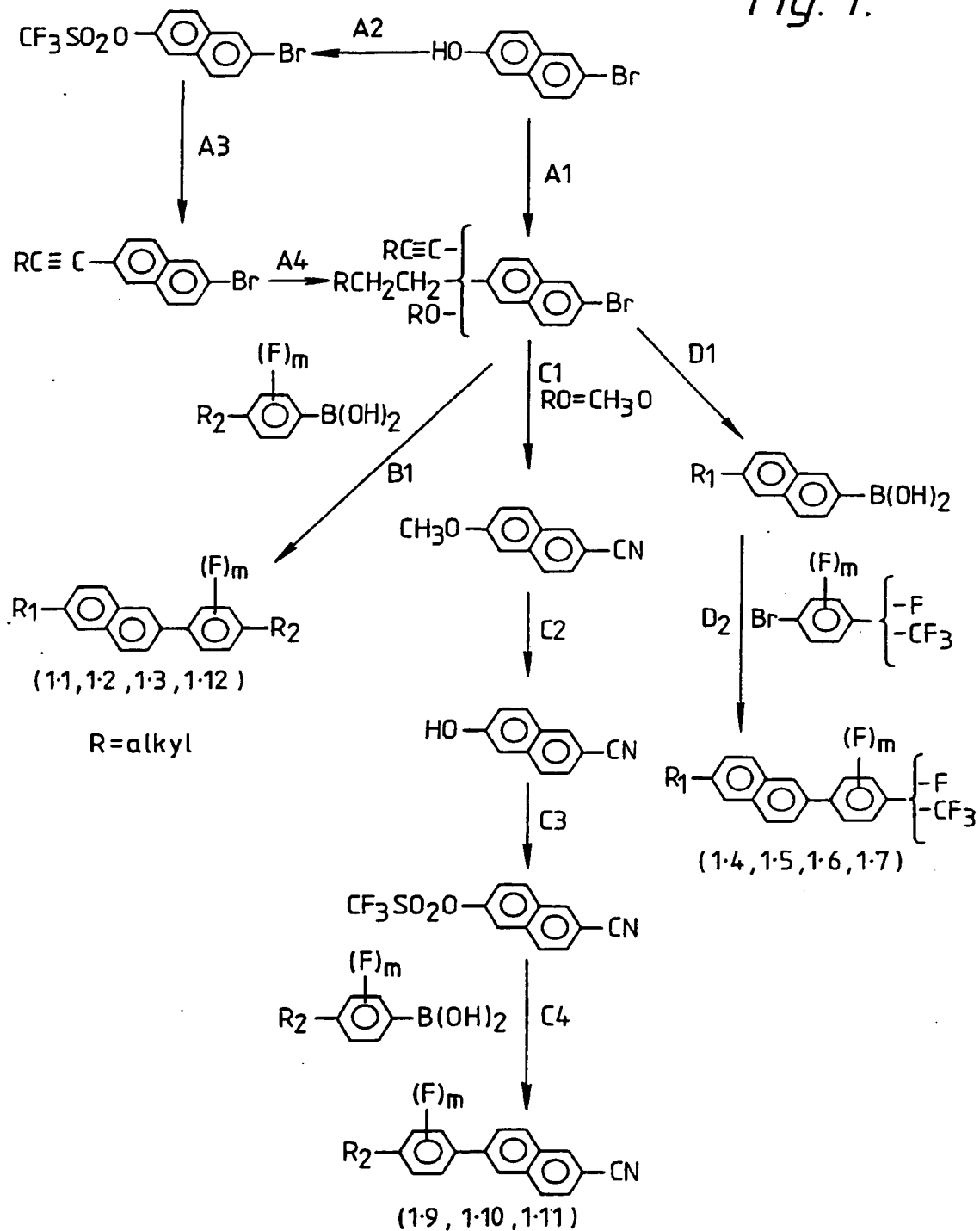
contains 50 - 95 weight % of compound(s) of formula IIA, IIB or IIC:



wherein R_A and R_B are independently C_{1-10} n-alkyl or n-alkoxy and (F) indicates that one of the rings carries a fluoro substituent.

16. Liquid crystal material according to Claim 14 characterised in that it is a ferro-electric chiral smectic C liquid crystal material that contains 1-99 weight % of phenylnaphthalene(s) of formula I in which R_1 and R_2 are selected from n-alkyl or n-alkoxyl and m is 1 or 2 and in that the material contains 1-20 weight % of optically active compound(s), the total being 100 weight %.
17. Material according to Claim 16 characterised in that m is 2, the fluorines being in the 2, 3 positions.

Fig. 1.

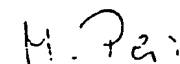


SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

PCT/GB 90/00069

International Application No.

| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply indicate all) According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 07 C 25/24, C 09 K 19/32, C 07 C 43/225, 255/54, 255/52 | | |
|---|---|--|
| II. FIELDS SEARCHED Minimum Documentation Searched ⁷ Classification System: IPC ⁵ Classification Symbols: C 07 C 25/00, 43/00, 255/00, C 09 K 19/00 Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched ⁸ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| Y | Helvetica Chimica Acta, volume 68, fasc. 5, 14 August 1985, U.H. Lauk et al.: "Synthese und flüssigkristalline Eigenschaften 2,6-disubstituierter Naphtaline", pages 1406-1426 see the whole article cited in the application -- | 1,14-17 |
| Y | Molecular Crystals and Liquid Crystals + Letters, volume 99, no. 1/4, 1983, Gordon & Breach, Science Publishers, Inc., (US) G.W. Gray et al.: "Synthesis and properties of some 2-n-Alkyl-6-(4'-cyanophenyl)-naphthalenes-3,4-dihydronaphthalenes, and -1,2,3,4-tetra-hydronaphthalenes", pages 123-138 see the whole article ----- | 1,14-17 |
| <p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search 17th April 1990 | | Date of Mailing of this International Search Report 22.05.90 |
| International Searching Authority EUROPEAN PATENT OFFICE | | Signature of Authorized Officer  |